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COMPLETE SPECIFICATION

Sealing Gaskets for Container Closures

We, W. R. GRACE & Co., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7 Hanover Square, New York 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to sealing gaskets for container closures, e.g. of the crown, roll-on thread, pre-threaded screw and lug types, and to their formation.

Sealing gaskets (which term includes "sealants" and "liners") have been made of a variety of materials including cork and paper wads and, for the so-called flowed-in or moulded gaskets, gelled plasticised polyvinyl chloride. Non-plasticised thermoplastic materials such as polyethylene, and copolymers of ethylene, have also been used.

We have now found that sealing gaskets having good sealing properties can be made from certain thermoplastic block copolymers, namely thermoplastic styrene-butadiene, and vinyl pyridine-butadiene, block copolymers, and from compositions comprising a thermoplastic styrene-butadiene block copolymer and a thermoplastic olefin polymer.

In one aspect the invention provides sealing gaskets for container closures comprising a thermoplastic material which is a block copolymer of styrene and butadiene, or a block copolymer of vinyl-pyridine and butadiene, or a composition comprising (a) a block copolymer of styrene and butadiene or of vinylpyridine and butadiene and (b) an olefin polymer. The term "olefin polymer" is used in this context throughout the specification to refer to a polymer of a hydrocarbon containing at least one carbon to carbon olefinic double bond, and includes homopolymers and copolymers formed from such a hydrocarbon.

In another aspect, the invention provides container closures comprising the gaskets of the invention.

The styrene-butadiene block copolymers useful in this invention preferably contain from 20% to 40% styrene and have styrene segments at each end of the polymer chain, and are generally prepared by addition polymerising butadiene with styrene in the presence of an alkyl lithium catalyst. They include those wherein the blocks derived from the butadiene comprise a saturated backbone carbon chain having vinyl substituents thereon. The styrene-butadiene block copolymers may or may not have been hydrogenated. Typical styrene-butadiene block copolymers are those available commercially under the Registered Trade Marks "Thermolastic" and Trade Names "Kraton" and "Pharos". These copolymers are not to be confused with the random copolymers of styrene and butadiene, which are well known as synthetic rubbers and which are not thermoplastic, or with the rigid high impact materials such as the styrene-butadiene graft copolymers or with blends of polystyrene with butadiene polymers.

The suitable thermoplastic vinyl pyridine-butadiene block copolymers are of much the same type and are described in British Specification No. 1,032,150. These polymers, which contain less than 40%, and preferably approximately 25% to 35%, vinyl pyridine, are hydrochlorinated, i.e. at least part of the vinyl pyridine blocks are in the form of the hydrochloride, rendering the polymers resistant both to oils and solvents. Thus these polymers are particularly advantageous in that gaskets prepared from them are oil and solvent resistant.

The olefin polymer in the compositions of the invention may be, for example, polystyrene or polyethylene, low density polyethylene being preferred. Olefin copolymers such as ethylene/vinyl acetate may also be used. The olefin polymer may be partially cross-linked (e.g. as a result of exposure

to high energy radiation), but it must be sufficiently thermoplastic to be mouldable on heating. Preferably, the compositions will contain up to 25% by weight of olefin polymer and at least 75% by weight of styrene-butadiene block copolymer.

By varying the proportions of olefin polymer and block copolymer present in the composition, it is possible to vary the physical properties of a gasket made therefrom. This is advantageous since gaskets having different characteristics and properties are required for different purposes. Thus, gaskets may be required which allow a low removal torque of the container closure, a high venting pressure, resistance to steam sterilisation, or resistance to solvents, such as ethanol in the case of closures for alcohol-containing packs, e.g. beer bottles.

In our copending Applications Nos. 12874/69 and 12888/69 (Serial No. 1196127) divided out of the present application, we have described and claimed thermoplastic compositions comprising (a) at least 75% by weight of a thermoplastic material which is a block copolymer of styrene and butadiene or a block copolymer of vinylpyridine and butadiene, and (b) up to 25% by weight of polystyrene, an ethylene-vinyl acetate copolymer or low density polyethylene. These compositions are especially preferred for making sealing gaskets for container closures.

Many methods are known for the production of sealing gaskets and their insertion in container closures. In our British Patent Application No. 1,112,023 we describe and claim a process for the production of gasketed container closures which includes introducing a pre-formed insert of a solid thermoplastic resilient material into a container closure which is warmed sufficiently to cause adequate adhesion of the insert to the closure, and moulding the insert under pressure to the required shape with a cold-moulding member or die, if necessary after further heating the closure. Such a process is termed "cold-moulding". The mould is preferably cooled by contact with a liquid coolant such as water.

In another process, a pellet of the gasket-forming material is compacted to a thin disc in the closure shell, reheated until it has partially reverted to its original shape and then cold-moulded to the desired final shape, if necessary after further heating the closure shell.

Other methods of forming gaskets include those in which the thermoplastic gasket-forming material is placed in the container closure, which may or may not have been preheated, and the material is subsequently heated and simultaneously or subsequently moulded. Plain or profiled gaskets may be formed depending on the profile of the moulding die.

The gaskets of the invention may be prepared from the thermoplastic material by any of the known methods. In order to facilitate the insertion of exactly the required quantity of sealant material into the closure before moulding to form the gasket, it is convenient that the sealant material be in the form of pellets or discs. Such discs and pellets may be obtained by conventional polymer processing techniques, e.g. by pressing the thermoplastic material into a thin sheet or tape, and then stamping or otherwise cutting the discs from the sheet or tape. Alternatively, the thermoplastic material may be extruded in the form of a rod, which may then be cut into small pieces or pellets. Before forming the gasket, a blowing agent may be incorporated in the sealant if cellular gaskets are to be formed.

The invention is illustrated by the following Examples.

Example 1

A styrene-butadiene block copolymer (sold under the trade mark "Pharos" 103 by the Shell Chemical Company) containing about 30% styrene and having styrene segments at each end of the polymer chain, was extruded in the form of a rod which was subsequently cut into small cylindrical pellets. The pellets were inserted into a warmed crown which was then passed under a series of radiant heaters. When the material had been heated sufficiently it was moulded with a cold mould into the desired gasket profile. The crowns thus formed showed excellent sealing and pressure retention properties.

Example 2

10 Parts of low density polyethylene were blended with 90 parts of the styrene-butadiene block copolymer described in Example 1 and the mixture was formed into a thin sheet. Discs were cut from the sheet and inserted into aluminium cap closures of the "roll-on" type, which were then heated. The softened polymer blend was then moulded with a cooled die to the gasket configuration described in our Belgian Patent Specification No. 704,553. The caps had excellent sealing characteristics and good pressure retention and torque removal properties.

Example 3

A blend of 20 parts low density polyethylene and 80 parts "Pharos" 103 were dry blended and extruded in the form of a rod 1 cm. in diameter. A pellet was cut from the rod and placed in the centre of a heated 31.5 mm. roll-on cap. The cap and pellet were further heated and then moulded with a cooled die as described in Example 2.

Example 4

20 Parts by weight polystyrene and 80 parts by weight styrene-butadiene block copolymer described in Example 1 were mixed together in a Banbury mixer. The mixture after sheeting on a two roll mill, was compression moulded into a sheet. Discs cut from this sheet were inserted into a warmed roll-on aluminium cap. The cap and disc were heated and the disc moulded with a cooled die. These caps had excellent sealing properties, good pressure retention with carbonated packs and low removal torque.

Example 5

A mixture containing 20% by weight partially cross-linked low density polyethylene (cross-linked by irradiation with high energy electrons at 10 megarads) and 80% by weight of the styrene-butadiene block copolymer described in Example 1 was prepared in a similar manner to that described in Example 4. Cap sealing gaskets were manufactured by the method described in Example 1 and showed good sealing properties, high pressure retention and gave low removal torques.

Example 6

80 Parts by weight of styrene-butadiene block copolymer described in Example 1 and 20 parts by weight low density polyethylene were blended together and extruded in the form of a rod 1 cm. in diameter. Pellets cut from the rod were inserted into a cap closure. After heating to soften the pellets they were impact moulded with a cold mould into thin discs. The cap and disc were then heated; during this heating the "elastic-memory" of the compound caused the disc partially to revert to pellet form. The pellet or disc was then moulded by a cold mould to give a shaped sealing gasket.

WHAT WE CLAIM IS:—

1. Sealing gaskets for container closures comprising a thermoplastic material which is a block copolymer of styrene and butadiene, or a block copolymer of vinylpyridine and butadiene.

2. Sealing gaskets according to Claim 1, wherein the block copolymer of styrene and butadiene contains from 20% to 40% styrene and has styrene segments at each end of the polymer chain.

3. Sealing gaskets according to Claim 1 or 2, wherein the block copolymer of styrene and butadiene is a hydrogenated copolymer.

4. Sealing gaskets according to any preceding claim comprising also an olefin polymer, (as hereinbefore defined) in admixture with the block copolymer.

5. Sealing gaskets according to Claim 4, wherein the olefin polymer is polyethylene, polystyrene, or an ethylene/vinyl acetate copolymer.

6. Sealing gaskets according to Claim 5, wherein the olefin polymer is low density polyethylene.

7. Sealing gaskets according to Claim 5, wherein the olefin polymer is a cross-linked polyethylene.

8. Sealing gaskets according to any one of Claims 4 to 7 wherein the thermoplastic material is a composition comprising up to 25% by weight of the olefin polymer and at least 75% by weight of the block copolymer.

9. Sealing gaskets according to Claim 1, substantially as hereinbefore described.

10. Sealing gaskets according to claim 1, substantially as described in any one of the Examples.

11. Container closures containing a sealing gasket as claimed in any preceding Claim.

12. Container closures according to Claim 11, substantially as hereinbefore described.

13. Process of forming sealing gaskets in container closures, as claimed in Claim 11, wherein a pellet of the gasket-forming material is compacted to a thin disc in the closure shell, reheated until it has partially reverted to its original shape, and then moulded under pressure to the desired final shape by a cold moulding member, if necessary after further heating the closure shell.

14. Process according to Claim 13, substantially as described in Example 6.

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